PART ONE
DIAROYL AND DIACYL QUINONE DIIMIDES

PART TWO
THE EFFECT OF ALPHA SUBSTITUENTS ON THE BEHAVIOR OF ALIPHATIC DIBASIC ACIDS

BY

JOHN LYNDE ANDERSON

B.Chem., University of Minnesota, 1947
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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PART ONE

DIAROYL AND DIACYL QUINONE DIIMIDES

Introduction

p-Quinone di-benzenesulfonimides were first prepared by A. S. Nagarkatti[1] in this laboratory. They are best synthesized by the oxidation of the corresponding *p*-phenylene di-benzenesulfonamides with lead tetraacetate in glacial acetic acid at room, or somewhat above room, temperature. These quinone diimides are stable, crystalline compounds which undergo many of the reactions of quinone itself. They add hydrogen chloride readily to give the monochloro-*p*-phenylene di-benzenesulfonamides and are readily reduced to the parent diamides by the usual reagents.

The present investigation was originally undertaken to prepare *p*-quinone monoimine monobenzenesulfonimides, but preliminary experiments indicated that these compounds are comparatively unstable. Then the formation of diacyl and diaroyl quinone diimides was realized for the first time. The purposes of this investigation were to synthesize various diacyl and diaroyl quinone diimides, to demonstrate the generality of this oxidative reaction, and to characterize the diimides by the formation of derivatives.

Discussion of Results

p-Quinone di-acetimide, di-benzimide, di-carbethoxyimide, di-ethoxalylimide, and monobenzimide monobenzenesulfonimide have been synthesized by the lead tetraacetate oxidation of the corresponding *p*-phenylene diamides using inert solvents such as benzene, chloroform, and ethyl ether. The yields in these reactions are adequate but are not as satisfactory as those in the di-benzenesulfonimide series.

The *p*-quinone diimides add hydrogen chloride readily, presumably by a 1,4 mechanism, to give the 2-chloro-*p*-

phenylene diamides in excellent yields. Only *p*-quinone diethoxalylimide does not add hydrogen chloride under the conditions used, that is, dry hydrogen chloride passed into a chloroform or petroleum ether solution of the diimide or addition of concentrated hydrochloric acid to a glacial acetic acid solution of the diimide.

2-Chloro-*p*-phenylene di-benzamide is easily oxidized by lead tetraacetate in refluxing benzene to the 2-chloro-*p*-quinone di-benzimide.

p-Quinone di-benzimide and *p*-quinone di-ethoxalylimide are reduced quantitatively to the *p*-phenylene diamides by sodium hydrosulfite. *p*-Quinone di-benzimide is reduced in 60% yield to the *p*-phenylene diamide by heating with aqueous sodium hydroxide.

The diaroyl quinone diimides are yellow, crystalline compounds which are comparable in stability to the di-sulfonimides. The di-acyl quinone diimides are also yellow but less stable and must be carefully purified prior to storage to prevent decomposition.

The solubilities of the quinone diimides are remarkably different from those of the parent *p*-phenylene diamides. The diimides are soluble in all the common organic solvents and are best recrystallized from ethyl ether and/or petroleum ether; the diamides are for the most part insoluble in the common organic solvents such as ethanol, benzene, ether, etc.

The infrared absorption spectra showed no characteristic quinoid peaks on preliminary examination. The ultraviolet absorption spectra also showed no characteristic quinone diimide absorption maxima which may have been due to the wide variance in the total conjugated systems.

The quinone diimides give characteristic color reactions with concentrated sulfuric acid.

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PART TWO

THE EFFECT OF ALPHA SUBSTITUENTS ON THE BEHAVIOR OF ALIPHATIC DIBASIC ACIDS

Introduction

Monomeric cyclic anhydrides are readily formed from succinic and glutaric acids but not from the homologous acids which would afford rings of less than five or more than six members. Auwers and Meyer (1,2,3) were the first to observe the influence of alpha substituents in the aliphatic dibasic acids in increasing the ease of formation and the stability of the corresponding succinic and glutaric acid anhydrides. Later Farmer and Kracovski (4,5) synthesized $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid and observed that it forms a monomeric anhydride whereas the unsubstituted adipic acid is converted under similar conditions to a polymeric anhydride.

The preparation of the cyclic anhydrides of the unsubstituted dibasic acids above glutaric acid was finally achieved by Hill and Carothers (6,7,8) using molecular distillation techniques. They found that pimelic through tetradecanedioic acids formed solid, polymeric anhydrides of molecular weights from 3000 to 5000 by heating with acetic anhydride. On molecular distillation these anhydrides underwent two changes: 1. The polymers on heating at very low pressures formed superpolymers of much higher molecular weight. 2. These polymers depolymerized slowly and yielded cyclic, monomeric anhydrides except that the polymeric anhydrides of suberic, sebacic, and dodecane dioic acids yielded only dimeric forms on distillation. In every case the cyclic monomers were unstable and repolymerized on warming to room

temperature as did the cyclic dimers on heating above their melting points.

The purposes of this investigation were to synthesize $\alpha,\alpha,\alpha',\alpha'$-tetrasubstituted dibasic acids of seven to fourteen carbon chain length and to determine the types of anhydrides formed, both by the usual chemical methods and by molecular distillation techniques.

Discussion of Results

The $\alpha,\alpha,\alpha',\alpha'$-tetramethyl- pimelic, suberic, azelaic, sebacic, undecanedioic, dodecanedioic, tridecanedioic, and tetradecanedioic acids were synthesized by the method of Haller and Bauer (9). The synthetic method involves the condensation of two moles of isobutyrophenone with one mole of a polymethylene bromide followed by sodium amide cleavage of the resultant dibenzoyl compound to the corresponding diamide. Hydrolysis of the diamide with nitrous acid gives the dibasic acid.

Heating these acids under reflux with a ten-fold excess of acetic anhydride followed by removal of the acetic acid and excess acetic anhydride *in vacuo* gave polymeric anhydrides in every case. This method of anhydride formation yielded a solid form in the case of the tetramethylpimelic acid, very viscous, liquid forms (molecular weights of 1000-2000) in the other seven acids. Solid polymeric forms which analyzed for pure anhydrides of approximately dimeric molecular weight were obtained by crystallization of the liquid forms of the suberic, sebacic, undecanedioic, and dodecanedioic acid anhydrides.

Molecular distillation of the liquid or solid forms gave monomeric, cyclic anhydrides in the cases of the tetramethylundecanedioic, dodecanedioic, tridecanedioic, and tetradecanedioic acids. Their monomeric nature was confirmed by the odors which were characteristic of the ring sizes (10), by molecular weight determinations using the cryoscopic method in benzene, by their analyses, and by the semi-quantitative

formation of monoamides by the reaction with liquid ammonia and sodium. The molecular distillation of the polymeric anhydrides of the tetramethyl-pimelic, suberic, azelaic, and sebacic acids gave as distillates mixtures of monomeric and dimeric cyclic anhydrides as shown by their analyses, molecular weights, and odors.

During the molecular distillations, part of the polymeric anhydrides being distilled were converted into very much higher molecular weight polymers as evidenced by the virtual insolubility of the residual material in the common organic solvents.

The monomeric cyclic anhydrides which were collected as a result of the molecular distillations were unstable, highly hygroscopic forms which lost their peculiar odor characteristics after standing in air overnight or in a desiccator for two or three days.

Attempted syntheses of the $\alpha,\alpha,\alpha',\alpha'$-tetraphenyl analogs of these acids by condensing polymethylene bromides with diphenylacetonitrile or ethyl diphenylacetate yielded the dinitriles and diesters in excellent yields. However, hydrolyses of these acid derivatives were not successful.

Conclusions

The presence of four methyl groups on the alpha carbon atoms of the aliphatic dibasic acids containing seven to fourteen carbon chains causes definite changes in the behavior of the acids. The polymeric anhydrides formed by heating with acetic anhydride are of very much lower molecular weight than those formed from the unsubstituted acids. The monomeric anhydrides which distill during molecular distillation are more stable than those from the unsubstituted acids; all the tetramethyl acid anhydrides distill, in part at least, as cyclic monomers. Thus the alpha methyl groups either promote ring formation or inhibit polymer formation or do both. However formation of monomeric or dimeric ring anhydrides exclusively was not realized in the tetramethyl

dibasic acid series studied in these investigations.

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VITA

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